571c In-Situ Ftir and Xas Study of the Evolution of Surface Species during Transient Co Oxidation on Supported Au/Tio2

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Au/TiO_2 catalyst prepared by deposition-precipitation of $HAuCl_4$, is remarkably active for CO oxidation at low temperature. The as-prepared catalyst is inactive; it is activated by contact with flowing H_2 at room temperature. Transient experiments involving the saturation of the catalyst either with CO or O_2, followed by admission of O_2 or CO, are performed. In-situ FTIR and XANES spectroscopy are used to monitor the development of surface species; the steady state CO oxidation activity of the catalyst is measured by gas phase FTIR. Exposure of the activated catalysts to 10 mbar of CO at -60 ^oC, leads to the formation of CO adsorbed species over only 13% of the gold. The process is verified by the development of a composite band at 2091 cm^{-1}, which is mainly due to CO adsorbed on Au^0 step sites close to the contact perimeter with the support. These species are very reactive toward CO_2 in the presence of oxygen; they can also be slowly removed by He, undergoing transformation to less labile adsorbed species as the CO coverage decreases. Purging of a CO-saturated catalyst with He, reduces the coverage of gold to 5% after 30 min. These less labile species appear at 2101 cm^{-1}; they correspond to CO adsorbed on step sites on top of the Au^0 particles.

Admission of 25 mbar of O_2 to the CO-saturated catalyst induces drastic changes on the nature and population of surface species. CO_2 is readily formed at the expense of the highly active CO-Au species (2091 cm^{-1}), at a TOF of 1.4 mol/mol Au-min. The 2091 cm^{-1} species are also simultaneously transformed into CO co-adsorbed with oxygen on the gold step sites, as evidenced by the development of a band centered at 2114 cm^{-1}. The contribution of the last species to the production of CO_2 is minor; they appear to act as a CO sink as the CO surface coverage decreases. XANES data show that the activation of CO by Au^0, which gives place to the CO-Au species characterized by the 2091 cm^{-1} band, is accompanied by a transfer of charge from Au^0 to CO; thereby, an increment in the white line in the x-ray absorption edge of Au is observed by exposure to CO. After admittance of O_2, gold returns to its zerovalent state at the time that CO is oxidized.

When CO flows through a catalyst previously saturated with O_2, a lag in the appearance of CO_2 is observed. CO_2 production is spread over a longer time scale, with a maximum TOF of 1 mol/mol Au-min. Whether the catalyst is initially saturated with CO or O_2 before admitting the other reactant, does not affect the total amount of CO_2 generated. Transformation of CO into CO_2 entails a hydroxocarbonyl intermediate characterized by an absorption band at 1240 cm^{-1}. Its rate of disappearing correlates with the rate of formation of CO_2. At steady state, CO_2 is generated at a TOF of 1.1 mol/mol Au-min, at a CO surface coverage of 10%, corresponding to 0.75 mol CO/mol surface Au. Oxygen co-adsorbs with CO on 3% of the available gold. All the results point to the main role of metallic Au as part of the active centers.